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Abstract:

The estimation of water and solute transit times in catchments is crucial for predicting the response of hydrosystems to external forcings (climatic or anthropogenic). The hydrogeochemical signatures of tracers (either natural or anthropogenic) in streams have been widely used to estimate transit times in catchments as they integrate the various processes at stake. However, most of these tracers are well suited for catchments with mean transit times lower than about 4-5 years. Since the second half of the 20th century, the intensification of agriculture led to a general increase of the nitrogen load in rivers. As nitrate is mainly transported by groundwater in agricultural catchments, this signal can be used to estimate transit times greater than several years, even if nitrate is not a conservative tracer. Conceptual hydrological models can be used to estimate catchment transit times provided their

consistency is demonstrated, based on their ability to simulate the stream chemical signatures at various time scales and catchment internal processes such as N storage in groundwater.

The objective of this study was to assess if a conceptual lumped model was able to simulate the observed patterns of nitrogen concentration, at various time scales, from seasonal to pluriannual and thus if it was relevant to estimate the nitrogen transit times in headwater catchments. A conceptual lumped model, representing shallow groundwater flow as two parallel linear stores with double porosity, and riparian processes by a constant nitrogen removal function, was applied on two paired agricultural catchments which belong to the Research Observatory ORE AgrHys. The Global Likelihood Uncertainty Estimation (GLUE) approach was used to estimate parameter values and uncertainties. The model performance was assessed on (i) its ability to simulate the contrasted patterns of stream flow and stream nitrate concentrations at seasonal and inter-annual time scales, (ii) its ability to simulate the patterns observed in groundwater at the same temporal scales, and (iii) the consistency of long-term simulations using the calibrated model and the general pattern of the nitrate concentration increase in the region since the beginning of the intensification of agriculture in the 1960s. The simulated nitrate transit times were found more sensitive to climate variability than to parameter uncertainty, and average values were found to be consistent with results from others studies in the same region involving modeling and groundwater dating.

This study shows that a simple model can be used to simulate the main dynamics of nitrogen in an intensively polluted catchment and then be used to estimate the transit times of these pollutants in the system which is crucial to guide mitigation plans design and assessment.

Keywords: lumped modeling, GLUE, surface water, shallow groundwater, hydro-chemical signatures, response times.

1. Introduction

The estimation of water and solute transit times in catchments is crucial for predicting the response of hydrosystems to external forcings (climatic or anthropogenic). As the hydrological and geochemical signatures of streams represent the integration of the various processes at stake (Aubert et al., 2013; Kirchner et al., 2001), they have been widely used to study hydrological processes and to estimate transit times in catchments. For example, many studies compute transit time distribution (TTD) by matching input (precipitation) and output (stream) time series of concentrations of natural tracers like stable isotopes ^{18}O and ^{2}H or chloride (McGuire et al., 2007). This method is well suited for catchments with mean transit times (MTT) lower than about 4-5 years (Hrachowitz et al., 2009; McDonnell et al., 2010), otherwise it can lead to large MTT underestimation (Stewart et al., 2010). However, it is more and more acknowledged that groundwater is playing a major role in nutrient transport in agricultural catchments leading to MTTs exceeding several years or decades, e.g. (Basu et al., 2012; Capell et al., 2012; Stewart et al., 2010). Several tracers of anthropogenic origin like ^{3}Hor CFCs can be used for estimating groundwater transit times spanning several decades, but the current decline in their concentration in the atmosphere increases the estimation uncertainty (Aquilina et al., 2012; Molénat et al., 2013; Stewart et al., 2010).

In many parts of the world, the intensification of agriculture led to dramatic increase of reactive nitrogen input to agricultural watersheds in the second half of the 20th century (Galloway et al., 2004). Agricultural inputs are known to be the main source of nitrogen in agricultural catchments (Dunn et al., 2012; Howden et al., 2011b; Wang et al., 2013; Worrall et al., 2012). This led to a general increase of the nitrogen load (mainly as nitrate) in many rivers of the world (Seitzinger et al., 2010, Green et al., 2014). However, using nitrogen for estimating catchment transit time is not straightforward as it is not a conservative tracer. Many studies on the impact of agriculture on stream nitrate concentration have enlightened the lack of correlation between estimated N inputs and outputs, but while part of them attribute this discrepancy mainly to N biotransformation, highlighting the attenuation potential of the system (Montreuil et al., 2010; Billen and Garnier, 1999), others suggest that it is mainly due to nitrate storage in the hydrosystem (vadose zone and groundwater) leading to response times exceeding several years even in very small catchments (Basu et al., 2012; Molenat et al., 2008; Owens et al., 2008; Ruiz et al., 2002a; Schilling and Spooner, 2006; Tomer and Burkart, 2003; Wriedt and Rode, 2006).

During the last 30 years, more and more complex hydrological models have been developed intending to simulate as accurately as possible the transformations and transfer of nitrogen in catchments, while accounting as much as possible for the spatial heterogeneity of the processes. However in models either semi-distributed, as INCA (Wade et al., 2002; Wade et al., 2001), SWAT (Arnold et al., 1998); or fully-distributed, as TNT2 (Beaujouan et al., 2001; Moreau et al., 2013);, MODFLOW-MT3D (McDonald and Harbaugh, 2003; Zheng et al., 2012) NitroScape (Duretz et al., 2011), the complexity brings a number of issues related to overparameterization, parameter uncertainty, and equifinality (Beven, 2006; Beven and Binley, 1992; Jakeman and Hornberger, 1993; Perrin et al., 2001). As a consequence, there is renewed interest for lumped conceptual models, as they are more parsimonious. However, the question remains if, while ignoring complexity and heterogeneity, such models are still able to mimic realistic catchment processes and to provide “the right answers for the right reasons” (Hrachowitz et al., 2013; Kirchner, 2006; Seibert and McDonnell, 2002).

A way to improve the realism of conceptual hydrological models is to make a better use of the available information while assessing model performances by not relying on stream data only but adding for example groundwater storage and chemical signature (Gupta et al., 2008; Seibert and McDonnell, 2002), although getting acceptable simulation on both stream flow and groundwater dynamics is not easy, even when considering only water (Fenicia et al., 2008; Gascuel-Odoux et al., 2010b; Molénat et al., 2005). Similarly, using the temporal variations of the hydro-chemical signature of streams can help in designing better model structures (Hrachowitz et al., 2011; Woodward et al., 2013).

In temperate climates, nitrate concentrations in streams are characterized by different time scales of variability. At the sub-daily scale, large variations can occur, which are linked either to hydrological events (storm events) or to diurnal biological processes. As groundwater is the main pathway for nitrate in agricultural catchments (Basu et al., 2012; Howden et al., 2011b; Molenat et al., 2008; Woodward et al., 2013) these variations are not likely to affect significantly the nitrate mean transit time. At the annual scale, seasonal cycles of nitrate concentrations are commonly described, either positively or negatively correlated with flow (Martin et al., 2006 ; Betton et al., 1991) and attributed mainly either to water mixing or to biological processes (e.g. Grimaldi et al., 2004; Martin et al., 2006; Woodward et al., 2013). Inter-annual variability reflects the combined influence of year-to-year variations of agricultural inputs and climate, the later determining the amount of water recharging the groundwater which impacts its transit times (Gascuel-Odoux et al., 2010a; Heidbüchel et al., 2013; Hrachowitz et al., 2009). On the long term (several decades), trends in nitrate concentration reflect the impact of agricultural system evolution. However, studies are generally focused on only one part of these temporal scales of variability. For example (Howden et al., 2011b) develop a model based on the long time series (140 years) of nitrate concentrations on the Thames River. The model is assessed on its ability to reproduce the dynamics of average yearly concentrations but without looking at the seasonal variations. Green et al. (2014) used simple models for simulated annual average nitrate concentrations over 10 catchments in USA and over the period 1964-2012, and estimated from the models the mean travel time of nitrogen in the catchments ranging between 0 and 19 years depending on the model and the catchment. However they did not consider seasonal pattern on the concentration too. Conversely, modelling seasonal variations of solute concentrations in streams is usually carried out using only one (Benettin et al., 2013) or a few (Woodward et al., 2013) water years.

The objective of this study was to assess if a conceptual lumped model was able to simulate the observed patterns of nitrogen concentration at various time scales from seasonal to pluriannual and thus if such a model was relevant to estimate the nitrogen transit time in headwater catchments. This was achieved using a 20 year time-series of stream base flow and nitrogen concentration on two paired agricultural catchments where a comprehensive survey of agriculture practices was available over the same period. The conceptual lumped model used (ETNA modified from (Ruiz et al., 2002b)) represents shallow groundwater flow as two parallel linear stores with double porosity, and riparian processes are represented by a constant nitrogen removal function. Parameter values and uncertainties were estimated using the Global Likelihood Uncertainty Estimation (GLUE) approach (Beven and Binley, 1992). The output variables of the model (water and nitrate output fluxes) were used to compute the nitrate residence times in both catchments. The model was assessed according to (i) its ability to simulate the contrasted patterns of stream flow and stream nitrate concentrations at seasonal and inter-annual time scales for the two catchments, (ii) its ability to simulate the patterns observed in groundwater (water level and chemistry) at the same temporal scales, and (iii) the consistency between the nitrate transit times resulting from the model calibration and the general pattern of the probable nitrate concentration evolution in the region since the beginning of the intensification of agriculture in the 1960s. Finally, the sensitivity of the simulated transit times to parameter uncertainty and climate variability was assessed and discussed by comparison with results obtained using other methods such as physically based models or groundwater dating with atmospheric tracers (CFCs).

2. Materials and methods

2.1 Study catchments

Kerbernez (11.5 ha) and Kerrien (10.5 ha) are two adjacent headwater catchments in South-western French Brittany (47°, 35' N; 117°52' E, see Figure 1). They belong to the Observatory for Research on Environment AgrHys (http://www6.inra.fr/ore_agrhys_eng/) which is part of the French network of catchments RBV (http://rnbv.ipgp.fr/). Elevations range from 14 to 38 m.a.s.l., and slopes are less than 8.5%. The climate is oceanic with mean annual temperature of 11.9°C, minimum of 5.9°C in winter and maximum of 17.9°C in summer. Both catchments are underlain by the same bedrock, a fissured and fractured granite, the “leucogranodiorite of Plomelin” (Bechennec and Hallegouet, 1999), overlain by a weathered regolith of 1 to more than 20 m depth. Soils are mainly sandy loam (dystric cambisol as per FAO classification) with an upper horizon rich in organic matter (4.5-6%). Soil depth proportions are given in Table 1. Soils are well drained except in the bottomlands which represent 1% and 7% of the total area in the Kerbernez and Kerrien catchments respectively.

Agriculture dominates the land use with 40% of the total area in Kerbernez catchment and 86% in Kerrien catchment. Urban area represents 27% of the Kerbernez catchment and 4% of the Kerrien catchment. Dairy farming is the major agricultural activity. On average over the period 1992-2012, in proportion of the total agricultural lands, grazed grasslands occupy 67% and 70% , maize 19% and 22%, and cereals 13% and 5% of the Kerrien and Kerbernez catchments respectively. Most of the grasslands are intensively grazed, and maize and cereals receive substantial amounts of fertilizers and manures.

2.2 Environmental and agricultural monitoring

Environmental and agricultural long-term time series are available at these sites. All the monitoring points are indicated on Figure 1. Meteorological data (rainfall, net solar radiation, air and soil temperatures, wind speed and direction) were recorded hourly since 1991 in an automatic weather station (CIMEL) and daily Penman PET was calculated. Mean annual rainfall over the period 1992-2012 is 1113 mm (+/-20%) and Mean annual Penman potential evapotranspiration (PET) is 700 mm (+/- 4%).

Stream discharge was calculated from water level measurements at the outlets using V-notch weirs equipped with a shaft encoder (OTT Thalimedes) recording every 10 min since 2000, and from weekly data recorded manually from 1997 to 2000. Water was sampled at the outlet since 1991 from 2 to 4 times a month. Mean annual runoff is 272 mm (+/- 45%) and 360 mm (+/- 60%) at the Kerbernez and Kerrien outlets respectively. In both catchments, base flow index is about 80 to 90%, thus the hillslope aquifer is the main contributor to the stream for both flow and nitrates export (Molenat et al., 2008; Ruiz et al., 2002a). The difference in runoff between the two catchments is attributed to differences in hydraulic conductivity of the regolith (Martin *et al.*, 2006).

Piezometers were drilled in 2000 along two transects (Martin et al., 2004). For this study, simulation results will be compared with the trends observed in upslope ($GW_{KB,Up}$ and $GW_{KN,Up}$) and midslope ($GW_{KB,Mid}$ and $GW_{KN,Mid}$) piezometers for Kerbernez and Kerrien catchments respectively. All piezometers consist of PVC tubes screened along the bottom meter of their length. The annular space around the tube was filled with sand in the screened zone, with bentonite above the screened zone and up to the last meter below ground surface, and then with concrete. This design aimed at allowing the determination of groundwater chemistry at a relatively precise sampling depth. Groundwater levels were monitored since 2001 either monthly if manual or every 15 min using vented pressure probes (OTT, Orpheus Mini). Water samples were collected in the piezometers, fortnightly during the recharge period and monthly otherwise, with an open bailer with a ball valve at the bottom. Purging was carried out every 3 months.

All water samples (stream and groundwater) were filtered in the field with a GNWP 0.45 µm filter and stored in the dark at 4°C. Nitrate concentrations were analyzed in the laboratory by ionic chromatography (Dionex).

An extensive survey of agricultural practices was carried out every year since 1992 to calculate the amount of annual N available for leaching on every agricultural plot of the site (Ruiz et al., 2002a). Collected data included the crop type, the amount and type of inorganic and organic fertilizers, the crop yields, management of crop residues and the dates of all technical operations. For grasslands, the proportion of legumes and the management of cattle grazing were documented.

2.3 Flux computation

2.3.1. Output fluxes computation

Daily stream flows were computed from the 10 min records. As this study is focused on base flow, individual storm events were discarded and base flow was estimated by linear interpolation. Instantaneous flow values were labeled as storm event when precipitations during the 24 previous hours were greater than 5 mm. This threshold and the 24-hour period were deduced from the analysis of the flood events (results not shown). Indeed, over the period 2001-2010, average flood event duration was about 12.5 hours, and the threshold of cumulated precipitation to induce a storm flow has been estimated around 5 mm. Annual water and NO_3-N fluxes were computed using a linear interpolation of NO_3 concentrations between two sampling dates, *i.e.* over 1 to 4 weeks. According to (Moatar and Meybeck, 2005), this method warrants an estimation of annual nitrate load with a precision ranging between 10 % (15 days sampling frequency) and 15 % (monthly sampling frequency) for their study site: the Loire River. Other comparison studies also showed that this method leads to a good compromise between error and biais (e.g. Zamyadi et al., 2007).

2.3.2. Soil Nitrogen balances computation

For arable land, the annual amount of N available for leaching was computed using the budget model proposed by COMIFER (1996) for France and parameters were modified according to regional references for the fate of N in organic fertilizers (Chauvin et al., 1997) and according to local references from lysimeter experiments carried out in the catchment to quantify the mineralization of soil organic matter (Simon and Le Corre, 1992). Positive budgets were then aggregated in each catchment for all the fields, to calculate the annual amount of N available for leaching at the catchment scale. More details about the method can be found in Ruiz et al. (2002a), but we modified the calculation for grazed grasslands and for mineralization following grassland destruction, by using the more recent model Territ'eau (Gascuel-Odoux et al., 2009) which is now used as a decision-support tool by stakeholders in the region (http://agro-transfert-bretagne.univ-rennes1.fr/Territ_Eau/)

Drainage and nitrogen leaching through the soils were simulated for each catchment using the annual N available for leaching for each catchment, meteorological data series (rainfall and PET), and soil properties (depth and water holding capacity) as input data, and using the Burns' model of nitrate leaching (Burns, 1975) at a daily time step. We considered soil layers 10 cm deep. Water holding capacity was set to 20 mm in the 30 first cm under soil surface, and to 15 mm below. The Burns model was applied at the scale of the catchment, by using the proportion of soil depths in the catchment area (Table 1).

2.4 Model rationale

2.4.1. Hydrology

In lumped models, the worth of using two reservoirs for simulating slow and fast groundwater components has been illustrated in several studies (e.g. Clark et al., 2009; Stewart et al., 2010; Woodward et al., 2013). In this paper, we used a modified version of the model ETNA (Ruiz et al., 2002b), which simulates water flow and nitrate concentrations at the outlet in base flow conditions as the result of two parallel linear groundwater reservoirs characterized by different recession coefficients α (in day^{-1}). A conceptual representation of this simple model is proposed in Figure 2. Each reservoir is fed by the drainage D (mm) computed using the Burns model (see section 2.3). The mobile water volume in each reservoir V_i (mm) and corresponding outflow Q_i (mm) are expressed as follows:

$$\boldsymbol{V_i(t) = V_i(t - dt) - Q_i(t - dt) + D(t)} \qquad \textit{(Eq. 1)}$$

$$\boldsymbol{Q_i(t) = \alpha_i V_i(t)} \qquad \textit{(Eq. 2)}$$

where t is the time (day), and dt the time step equal to 1 day.

Both study catchments lie on a deep regolith layer which allows a deep groundwater flow below the catchment outlets, leading to a systematic deficit in the water annual balance. This is accounted for in the model by the parameter f_l (in %) representing the proportion of deep losses. A pond has been settled in 2006 near the outlet of the Kerbernez catchment, and is partly draining the stream flow. It explains the difference of minimal base flow values after this date. Therefore the value of f_l was calculated from the difference between observed discharge and computed recharge (Burns model) on the period 2001-2011 and 2007-2011 for Kerrien and Kerbernez catchments respectively. It was 57.35% and 54.55% for Kerrien and Kerbernez catchments respectively. For all the calibrations on stream flow values, we considered only this latest period of the data series for both catchments. The stream flow is the combination of the contributions of the two groundwater reservoirs which evolve independently. The relative part of each reservoir (f_{fast} and 1-f_{fast}) is specific to each catchment. Considering the deep losses and the 2 reservoir contributions, the stream flow is finally computed as:

$$\boldsymbol{Q(t) = (1 - f_l)\left(f_{fast}Q_{fast}(t) + \left(1 - f_{fast}\right)Q_{slow}(t)\right)} \qquad \textit{(Eq. 3)}$$

where Q is the stream flow, Q_{fast} and Q_{slow} the outflow from fast and slow stores respectively, all expressed in mm.day^{-1}.

2.4.2. Nitrogen transfer

Nitrogen input to each reservoir is the daily nitrogen leaching L (kg N.ha^{-1}) computed using the Burns model (see section 2.3.2). To take into account the microporosity of the regolith, a constant immobile volume of water was considered. We assumed a complete mixing between mobile and immobile water within a day, leading to the following equation for each store:

$$\boldsymbol{C_i(t) = k\frac{S_{Ni}(t-dt) + L(t) - Q_i(t-dt)C_i(t-dt)}{V_i(t) + V_{im,i}}} \qquad \textit{(Eq. 4)}$$

$$\boldsymbol{S_{Ni}(t) = C_i(t)\left(V_i(t) + V_{im,i}\right)} \qquad \textit{(Eq. 5)}$$

where for each reservoir i, S_{Ni} is the N storage, (kg N.ha^{-1}), $V_{im,i}$ the immobile volume (mm) and C_i the concentration (in mg NO_3.L^{-1}). k is a mass conversion factor (from kg N.ha^{-1} to mg NO_3.L^{-1}, k=443).

The daily concentration at the outlet (C_{out}, in mg NO_3.L^{-1}) is then computed according to the relative contribution of the 2 reservoirs:

$$C_{out}(t) = \frac{(1-f_l)(f_{fast}C_{fast}(t)Q_{fast}(t)+(1-f_{fast})C_{slow}(t)Q_{slow}(t))}{Q(t)} \quad (Eq.\ 6)$$

The nitrate concentration of the deep losses is assumed to be equal to the concentration at the outlet. Denitrification has been largely investigated in various surface reducing environments. It has also been assumed in groundwater, once oxygen concentrations have decreased. However no transformation is assumed to occur in the groundwater or in the unsaturated zone, the main raison being the high dissolved oxygen content of groundwater in the region (Bidois, 1999). In the study site, the average concentration is about 5 mg of dissolved O_2/l (unpublished data).Indeed, a regional investigation of groundwater ages and nitrate concentrations (Aquilina et al., 2012) showed only limited evidences for denitrification. Evidences for denitrification were observed in the region only in specific environments such as pyrite-rich schists (Pauwels et al. 2000) or in sites influenced by pumping (Tarits et al., 2006). One explanation might be related to the passivation of reactive surfaces of reduced minerals inhibiting autotrophic denitrification processes. In the Kerrien and Kerbernez catchments, although potential denitrification was assumed in the unsaturated zone (Legout et al., 2005) no denitrification process has been evidence through chemical or isotopic analysis (Martin et al., 2004; Pierson-Wickmann et al., 2009).

2.4.3. Nitrogen transformation in the riparian-riverine zone

The biological transformation of nitrate, either by denitrification in the wetlands or stream consumption by aquatic primary producers was simulated as a constant daily amount of nitrate removal R_c (kg N.ha^{-1}.day^{-1}). Main limiting factors are known to be the nitrate availability, the temperature, the soil moisture, and light (Billen et al., 1994; Oehler et al., 2009). These factors vary seasonally and to some extent are likely to compensate each other, e.g. in winter, wetland saturation favors the occurrence of anoxic conditions and nitrogen concentration are often larger, while in summer temperature and light intensity favor biological activity. In addition, even if nitrate removal was higher in winter, the effect on nitrate concentration would be negligible considering the large nitrate load. Thus, simulating biological removal as a constant appeared as a reasonable parsimonious assumption. The stream nitrates concentration was finally computed as:

$$\boldsymbol{C(t)} = \frac{\mathrm{Max}[\boldsymbol{kC_{out}(t)Q(t)-R_c;0}]}{\boldsymbol{Q(t)}} \qquad \textit{(Eq. 7)}$$

The model was run using a Matlab® code (R2008a version).

2.5 Model calibration

In order to optimize the parameter set values and determine the associated uncertainties, we applied the Global Likelihood Uncertainty Estimation (GLUE) framework proposed by (Beven and Binley, 1992). The GLUE method is an uncertainty analysis technique inspired from Bayesian averaging of models and predictions, *i.e.* where a prior distribution of models is assessed in terms of some likelihood measure relative to the observations, and a posterior distribution is then calculated (Beven and Freer, 2001). A preliminary manual calibration was performed, and allowed us to define a prior range of values for each parameter. The initial conditions were fixed at this stage and were not integrated into the GLUE procedure, as a preliminary test showed that they have little impact on GLUE results. Then 10,000 runs were performed using a random uniform sampling procedure (as no prior knowledge was available on the parameter distributions). The independent calibration for each catchment resulted in large uncertainties of the 6 calibration parameters. To reduce this uncertainty we calibrated the model simultaneously on the two catchments, using combined likelihood and assuming that only two parameters can vary between the two catchment: the proportion of fast store (f_{fast}) and the nitrate removal constant (R_c). The recession coefficients in each store (α_f and α_s) and the immobile volumes in each store ($V_{im,f}$ and $V_{im,s}$), which are intrinsic characteristics of the regolith aquifer, were assumed to have the same value in both catchments. This assumption was supported by previous model calibrations for these sites (Ruiz et al., 2002b) and seems reasonable in the case of neighboring catchments in the same geological context. Calibration was carried out in two steps, adjusting first the hydrological parameters (α_f, α_s, $f_{fast,KRN}$ $f_{fast,KBZ}$) only, and then the parameters related to the N transformations and transfers ($V_{im,f}$, $V_{im,s}$, $R_{C\ KRN}$ $R_{C\ KBZ}$).

Several performance criteria based on the distance between simulated and observed values were tested to build the objective functions (OF). The mean absolute error (MAE), which is a classical standard in model performance assessment (Bennett et al., 2013) was finally selected.

We chose to apply this criterion on the square root rather than on the absolute value of stream flow as our simplified model does not simulate the flood events but only the base flow dynamics. For a detailed discussion on this point, one can see in Pushpalatha et al. (2012) a study of the relevance of a range of classical criteria in hydrology to assess the performance of models in reproducing low flow or medium flow. For the nitrogen related components of the model, the same criterion, applied on the square root of nitrate concentrations, was also found to be the most relevant.

The MAE is always greater than 0 and tends to infinity as the discrepancy between model and observations increases. An objective function (*OF*) value for each catchment *j* and each parameter set θ was obtained by taking the inverse of the normalized MAE so that the *OF* increases with the model performance:

$$\boldsymbol{OF^j(\theta)} = \left(\frac{\boldsymbol{MAE^j\ (\theta)}}{\sum_\theta \boldsymbol{MAE^j\ (\theta)}}\right)^{-1} \qquad (Eq.\ 8)$$

For each calibration step, the combined likelihoods, *CL (θ)*, were computed as the product of the objective functions obtained for both catchments divided by their sum for all explored parameter sets:

$$OF\ \ (\theta) = \prod_{j=1}^{nb\ of\ catchments} OF^j(\theta) \qquad (Eq.\ 9)$$

$$CL\ \ (\theta) = \frac{OF\ \ (\theta)}{\sum_\theta OF\ \ (\theta)} \qquad (Eq.\ 10)$$

Thus, the combined likelihoods are between 0 and 1 and increase with the model performance.

The 0.1% of the running sets giving the best CL was selected as behavioral parameter sets. The optimal value of each parameter was taken from the average of the behavioral set values, and the uncertainty was computed as the relative standard deviation of the behavioral set values.

2.6 Evaluation of model consistency on groundwater observations and long time series

We evaluated the model consistency on its ability at simulating the groundwater dynamics, and then its compatibility with realistic long-term evolution trends. To compare simulated groundwater storage to observed water table levels in piezometers, simulated water table levels were calculated from the simulated content of water in the two reservoirs and by using a value of 1.5% for the specific yield of the regolith, that was found on is this site by Martin et al., (2006), and a maximum mobile volume of groundwater of 650 mm. The average daily simulated water table levels were calculated as follow:

$$Z_{sim}(t) = -1/0.015\left(650 - \left(f_{fast}V_{fast}(t) + \left(1 - f_{fast}\right)V_{slow}(t)\right)\right) \qquad \textit{(Eq.11)}$$

In order to test if such a simple lumped model, calibrated only on recent years, could simulate realistic dynamics over a longer period, the model was applied on both catchments for the period 1965-2011, corresponding to the full available meteorological time series on the site, using the mean behavioral parameter set. We considered that starting the simulation with nitrate-free reservoirs in 1965 was realistic as all available regional data on stream nitrate concentration before 1975 display very small values, all smaller than 10 mg NO_3/L (Aquilina et al., 2012). As mentioned earlier, no quantitative information on the agricultural practices in the catchment is available before 1992. Regional or national statistics are difficult to downscale for our headwater catchments, which comprise only few plots. Therefore, we generated time series of annual N available for leaching using very simple assumptions relying on historical regional statistics (Aquilina et al., 2012) and qualitative information on the studied catchments.

Although no quantitative agricultural data is available before 1992, interviews with farmers revealed that while in the Kerrien catchment, farming has been consistently primarily dedicated to dairy production at least since the 50's, the Kerbernez catchment used to host a farm with very intensive pig production. The main agricultural field in this farm was devoted to outdoor sows. Farm buildings included indoor pigs for fattening, pig slurry being spread mostly in the catchment itself before 1990. The pig production decreased progressively. Outdoor sows stopped in the 80's and indoor pigs declined slowly in the 90's until 2000 when the farm ceased its activity and its agricultural fields were allocated to neighboring dairy farms.

The simplest evolution which can be generated is a linear increase of annual N available for leaching starting at zero in 1965, and increasing until 1992, as a result of the increase of N fertilizers and animal production. This simple scenario was applied on the Kerrien catchment as we know that it was consistently dominated by dairy farming throughout the period. The slope of the increase was adjusted to fit the observed concentration at the outlet at the beginning of the observation period in 1992. Figure 3 presents the full time series of annual N available for leaching, with estimated values from 1965 to 1991 and observed values after 1992.

For the Kerbernez catchment, the observed seasonal dynamics (inverse correlation between stream flows and nitrate concentrations) imposed that the slow store must be more concentrated in nitrate than the fast store in the latest period. Considering the model structure, this was possible only if the annual N available for leaching had increased dramatically in the initial period, and then started decreasing before 1992. This was consistent with the qualitative information collected in this catchment that revealed the early development of pig intensive breeding and its progressive decline since the 1980s. The two slopes of these successive trends of annual N available for leaching, starting at zero in 1965, were therefore adjusted to reach the observed concentration in 1992. The full time series (Figure 3) showed that the adjustment led to very high values of annual N available for leaching in the 60s. These high values might not been realistic, and a smoother, more plausible scenario might have been designed, for example by introducing three successive trends (increase, stabilization, decrease). However, as no data were available to constrain such a scenario, and as the simulated concentrations in the latest period were little sensitive to the distribution of annual N available for leaching in the early period, this option was discarded.

2.7 Nitrate transit time calculations

Transit time distribution of water or solutes is the result of the highly variable flow pathways followed by individual molecules in catchment. While being often considered as an intrinsic property of a catchment, transit times are also depending on the climatic conditions.

The calibrated models were used to estimate the transit time of nitrogen in each catchment for the observed climate time series 1965-2012, by simulating the time needed for a pulse of nitrate (a single day pulse input of nitrate in a nitrate-free system) to exit the catchment. For this exercise, the parameter for nitrates removal (R_c) was set at zero, to ensure a conservative behavior of nitrate, and nitrate output was calculated as the sum of stream and deep loss outputs. In order to estimate the sensitivity of transit time estimations to climatic conditions, three dates for the nitrate input pulses were selected in the observed climatic time series, on 1st of August 1968, 1974 and 1980, representative of dry, average and wet climatic sequences respectively. For each of these cases, the model was run for each of the behavioral sets of parameters so that it was possible to estimate the sensitivity of the nitrogen transit time to parameter uncertainties. It has to be noted that as the estimated transit time assumes conservative transport of nitrate and consider all nitrate leaving the system, and may differ from actual transit time of nitrate leaving the system specifically via the streams.

The transit time distribution can be represented as the evolution with time of the cumulated fraction of recovered tracer in output flux. The Mean Transit Time (MTT) is the most commonly used proxy for this distribution but as a full tracer recovery is needed to calculate it, it frequently imposes a repetition of available climate time series, e.g. (Dunn et al., 2007). However water transit time and nitrate transit times may differ slightly depending on the flow pathways taken by the nitrate molecules, e.g. in the study catchments storm events are a fast flow pathway responsible for the lowest values in the water transit time distribution curves while they are nitrate free as storm runoff occurs mainly over saturated area and so when nitrate has already been infiltrated (*e.g*. Aubert et al., 2013). As we wanted to characterize the effect of real climate on nitrate transit time estimations, we rather used Half Nitrogen Recovery Time (HNRT), which correspond to the times required to recover half of the nitrate introduced with the input pulse. Values of HNRT are slightly smaller than MTT when the distribution presents "long tails", but they still can be used to compare with groundwater MTT found in the literature.

3 Results and discussion

3.1 Model calibration

The simultaneous calibration of the model on the two paired watersheds using the GLUE methodology, on 8 parameters using 4 observed times series (stream discharge and nitrate concentration for the two catchments) led to a reasonably low uncertainty on parameters estimation (Table 2, Figure 4). The parameters describing the aquifer properties (α_f, α_s $V_{im,f}$, $V_{im,s}$) appeared well constrained with an uncertainty of about 10%. The removal constants R_c, are more uncertain especially in the Kerrien catchment, but their values being very low, they have little impact on the stream concentration except during very low flow periods. The proportion of fast store f_{fast} in each catchment, which controls the contrast between the catchment responses, reflects the more reactive nature of Kerrien compared to Kerbernez. For Kerrien, the behavioral value of f_{fast} tends to the upper bound which has been fixed to impose a maximum of 90% of each store, and its uncertainty is also relatively large.

Model performance was assessed with classical statistical criteria (Dawson et al., 2007): the Nash Sutcliffe Efficiency criteria on square root discharge were 0.73 and 0.81, and the root mean square error on concentration were 8.5 and 13.9 $mg.l^{-1}$ for Kerrien and Kerbernez catchments respectively. The simulated ranges of base flow discharge and nitrate concentration corresponding to behavioral parameter sets were relatively narrows (Figure 5). For discharge, they fit better the medium and low flow values than the high flow values, which is linked to the properties of the criterion used in the objective function. For nitrate concentration, simulated seasonal variations obtained with behavioral sets were in good agreement with the observed ones in the two catchment (Figure 5), both in terms of dynamics (cycles with flow-concentration relationship that are negative in Kerbernez and positive in Kerrien) (Martin et al., 2006) and in terms of amplitude, Kerbernez being more buffered than Kerrien catchment. In the model, these seasonal patterns in nitrate concentrations were mostly reflecting the nitrogen status of the catchments, through the relative nitrate concentrations in fast and slow stores indicating whether in the long term the groundwater N storage was increasing (Kerrien) or decreasing (Kerbernez). Nitrate removal was not affecting noticeably the concentration dynamics except during very low flows periods in Kerrien catchment, and had very little effect on nitrate load, the removal of nitrogen representing less than 1% of the total nitrogen output flux on the whole period. The observed interannual trends were also reasonably well reproduced by the simulations in both catchments. In Kerrien, concentrations increased slightly during the first years, declined markedly from 2000 to 2004, increased again up to 2007 and finally declined slightly. In Kerbernez, the concentration declined markedly along the whole period, except for a period of relative stabilization between 2003 and 2008.

However, when looking closely at yearly fit between observed and simulated concentrations, some discrepancies appeared which can be due to the model itself and also to errors in measurements of outputs and on forcing variables. Uncertainties on input data are crucial, especially when these data are coming from agricultural practices estimation. (Howden et al., 2011a) show that their model ability to simulate long-term nutrients concentration depends principally on the precision on the sources. In our work, we did not study specifically the uncertainty on the input data and its propagation on the model outputs. The comprehensive agricultural survey led to estimations of annual N available for leaching that were consistent with lysimetry studies performed in the same site (Simon and Le Corre, 1992). However, as the Burns model simulates highly variable inputs of nitrogen leaching during the whole recharge period, this could impose large values of immobile volume in groundwater stores for buffering this variability. To test this hypothesis, an additional calibration with GLUE was tested, using the same annual N available for leaching but constant annual concentrations of nitrates in the drainage water. Optimal parameter values and associated uncertainties were finally not significantly different (results not shown), indicating that the model was more sensitive to the average of N input over several years than to short term variations.

It is worth noting that discrepancies were often linked with inaccurate simulations of discharge (e.g in the years 2005 and 2006 in the Kerrien catchment, where the largely overestimated nitrate concentrations corresponded to largely overestimated stream discharges). Calibration on each catchment independently would have provided a slightly better fit, but at the cost of a much larger parameter uncertainty (results not shown). This highlights the difficulty of model calibration procedures to deal with seasonality. Most calibration effort in hydrology has been made on reproducing peak flows, often event per event, and we miss relevant metrics to include seasonal as well as inter-annual trends in performance criteria. The difficulty to find behavioral parameterizations fitting pluriannual and seasonal trends simultaneously has been raised by (Choi and Beven, 2007). When dealing with water quality, it becomes even more complex as its seasonality is related to the combined dynamics of stream flow and solute transport. For example, in periods when discharge is not well simulated, we should expect that a behavioral model would badly simulate the concentrations, while calibration procedures will favor models that tend to compensate the error on discharge by minimizing the concentration seasonality. This study showed that calibrating the model simultaneously on two catchments displaying contrasted seasonal patterns in concentration was one way of addressing this problem. The fact that it resulted in only one parameter (f_{fast}) controlling the contrast between the catchment responses is also interesting, as this parameter could serve as a useful metric to compare catchments in homogeneous geological contexts.

3.2 Assessment of model consistency

The model consistency was assessed first by comparing simulated groundwater storage and nitrate concentration with observed water level and nitrate concentration in piezometers then by testing its capacity to represent realistically long term trends in nitrate concentration.

The observed nitrate concentration displayed contrasted dynamics according to the piezometer location, as shown in Figure 6 only for two piezometers in each catchment for the sake of clarity. This spatial variability, both vertical and lateral has been highlighted in (Legout et al., 2007; Rouxel et al., 2011) in the same site. Simulations with the lumped model were not expected to fit individual piezometers. This is one of the limits of using the same parameterization for the regolith properties, here the specific yield, for the two catchments. However, comparing daily water table levels observed in the upslope piezometers and simulated with the mean behavioral parameter set provided interesting insights about the modeled behavior in the groundwater. Figure 6 showed that groundwater dynamics were better reproduced for Kerbernez than for Kerrien. Simulated concentrations were also showing contrasted dynamics in the different stores, the fast stores displaying more marked seasonality and larger year to year variations. Interestingly, concentrations dynamics observed in the hillslope appeared in good agreement with simulations of the fast store in Kerrien catchment, and with simulations of the slow store in Kerbernez catchment. Therefore, these results confirmed the consistency of the conceptual representation of the system, which led to calibrated groundwater system largely dominated by the fast store in Kerrien and by the slow store in Kerbernez.

Considering the very large immobile water volumes in each store resulting from the calibration (Table 2), it was crucial to test if the resulting very large memory effect was compatible with long-term trends of nitrate increase since the beginning of agriculture intensification. The long-term simulations on the two catchments (Figure 7) based on the reconstructed times series of annual N available for leaching (Figure 3) and using the mean behavioral parameter set, confirmed that the calibrated models were reactive enough to reach the range of concentrations observed in 1992 even when starting with a nitrogen free system in 1965. The concentrations in both groundwater stores obtained in 1992 with these scenarios were close to the initial values that were imposed in the calibration process for the two catchments (Table 3), leading to simulations of the years following 1992 that were very close to the ones obtained during calibration, in particular on Kerrien catchment.

Figure 8 also illustrates the asynchronic dynamics of the simulated nitrate concentration in the fast and slow groundwater stores, which are responsible for the seasonal patterns of nitrate concentration in the stream. In the Kerbernez catchment, the inversion of concentrations between fast and slow stores in the late 1980s, induced by the specific agricultural history of this site, led to the inversion of the seasonal patterns of nitrate concentration in the stream in the later period.

These results showed that a simple conceptual lumped model, while remaining parsimonious and allowing for a low uncertainty in parameter estimation, was not only able to simulate the observed patterns of nitrogen variations at various time scales, from seasonal to pluriannual, but also proved its consistency with respected to groundwater signature and long term behavior. This confirmed the relevance of using parallel linear stores to represent groundwater in lumped conceptual models, e.g. (Clark et al., 2009; Stewart et al., 2010; Woodward et al., 2013).

3.4 Nitrate groundwater transit time

The evolution with time of the cumulated fraction of tracer output flux for the range of the behavioral parameters (Figure 8) shows that for the explored time series, the full tracer recovery was attained after about 30 years for the Kerrien catchment while it was not attained even after more than 40 years for the Kerbernez catchment, confirming that calculations of mean transit time was not possible in this catchment using the available weather time series. The Table 4 shows that the average Half Nitrogen Recovery Time (HNRT) was smaller in the Kerrien catchment than in the Kerbernez catchment, while their variability was in the same range. Considering each pulse input date separately reduced the standard deviation of HNRT in Kerrien and not in Kerbernez, showing that in the Kerrien catchment, HNRT were more sensitive to the date of the pulse input than to parameter uncertainty, while for the Kerbernez catchment both factors had a similar influence. In terms of policy, it means that the time required to recover a good water quality will on such catchments is going to be very long and strongly dependent on the meteorological conditions. Dry years will tend to increase the time of nitrate storage in the catchment and then the recovery of low concentration levels in streams. Moreover, in catchments characterized by longer nitrate transit times (as the Kerbernez catchment) the predictions of N recovery under mitigation scenarios will be more uncertain.

These results are consistent with a previous study in the same catchments which estimate from the physically based model MODFLOW-MT3D that the reaction times required for equilibrating shallow and deep parts of the aquifer were between 6 and 8 years for Kerrien catchment, and between 10 and 12 for Kerbernez catchment (Martin et al., 2006). (Molenat and Gascuel-Odoux, 2002) estimate that transit times in a similar site (Kervidy-Naizin, also part of the ORE AgrHys) is ranging between 0 and 3 years, while arguing that it was still underestimated due to the fact that molecular diffusion between macro and micro porosity was neglected, and because their estimation was based on hydraulic gradients during winter high flows. A regional study using groundwater dating based on CFC tracers, including some samples belonging to Kerrien and Kerbernez catchments, also found water ages within the weathered aquifer that ranged between almost 0 to 20-25 years, with a mean of 18 years (Ayraud et al., 2008). Although these studies are referring to different “times definitions” like “reaction catchment times”, “catchment mean transit times”, or “groundwater age”, it is worth noting that all these estimates are spanning the same range of values, which is larger than one year and closer to the decade.

3.5 Limitations and perspectives for generalization

This work was based on very densely-monitored catchments, allowing to compare our model results to various environmental variables (surface and groundwater), on long-term time series, and to calibrate the model for two contrasted catchments simultaneously. The applicability of the approach for catchments where monitoring is scarcer, particularly regarding surveys of agricultural practices, is still to be tested. However, as we have shown that when nitrate transit time was large, the model was not very sensitive to short term variations of nitrate leaching, rough estimations of agricultural inputs might be enough to estimate catchment transit times with our approach.

The approach presented here is not restricted to the specific conceptual model that used in this study, which is relevant for the case of headwater catchments where the hillslope groundwater is the main contributor to the stream flow (Ruiz et al., 2002b). From the hydrological point of view, to deal with other geological or climatic contexts or poorly gauged catchments, some adjustments may be required. To achieve this, promising tools have been developed over the PUB decade (Hrachowitz et al., 2013). To cite just a few examples of them (Gharari et al., 2011) proposed some approach for model design based on catchment physical properties. (Fenicia et al., 2011; Kavetski and Fenicia, 2011) develop a flexible modeling approach to design improved conceptual models in adequation with the data that are available to constraint it, and with multi-objective performance criteria (Euser et al., 2013). Hrachowitz et al. (2014) highlighted how an iterative procedure of increasing process complexity associated with the systematic use of catchment signatures, expert knowledge, and realism constraints may guide the stepwise improvement of conceptual rainfall-runoff model to increase its consistency.

Application on larger scales may also require some refined formulation of N transformation model. (Montreuil et al., 2010) estimated that for order-6 streams in a similar context (Scorff basin, West

Brittany, France), up to 53 % of the annual nitrate flux during base flow can be removed within the wetland or in the river. (Flipo et al., 2007) estimated, by using mean annual N balance over a 1200 km^2 catchment, that 20% of the nitrate flux leaving the root zone was removed by denitrification. In such contexts, one can assume that riparian or in-stream transformations would induce a superimposed seasonal cycle on nitrate concentration which would require more process-based formalisms to discriminate the hydrological effect from the effect of others environmental factors. For example, denitrification may involve some controls by the water saturation dynamics, temperature, and the availability of substrates in wetlands (Pinay et al., 2007), while in-stream processes will depend on the amount of nitrates, light, temperature conditions, and other nutrient conditions (Garnier et al., 1995).

Nevertheless, the aim of this study was to assess the ability of such lumped models to provide valuable estimates of transit times of agricultural-derived pollutants as nitrates within headwater catchments in spite of parameter uncertainty and according to climate variability, and it proved their interest when considering simultaneously contrasted catchments. In such an approach, the degree of model complexity has to be consistent with the degree of contrast between the catchments, i.e. the number of relevant processes which have to be represented.

4 Conclusion

In the present study, we showed that time series of nitrate concentration in streams can be used to estimate nitrate transit times of more than several years in headwater catchments, by using a lumped and parsimonious model. The performance and consistency of the model ETNA was found adequate considering its ability to reproduce the nitrate concentration patterns (i) at different temporal scales (seasonal and inter annual), (ii) both in the stream and the groundwater and (iii) for the expected trends over several decades.

The GLUE approach was used to assess the parameter uncertainties and the subsequent uncertainties on nitrogen transit times by calibrating ETNA on two paired research catchments where contrasted chemical signatures are observed on a 20-year-period. Reasonably low parameter uncertainties were obtained by calibrating simultaneously the two catchments. The effect of parameter uncertainty on transit time estimations was in the same range as the effect of the climatic variability. The estimated nitrate transit times were found consistent with results from other studies in the same site or in the same region. Finally, only one parameter controlled the contrast in nitrogen transit times between the 2 catchments, which could constitute a simple metric for comparing catchments behavior in the same geological context.

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Table 1: Soil depth proportions in the two catchments

	Proportions of soils depth in the catchment	
Soil Depth	Kerrien	Kerbernez
Less than 40 cm	33%	17%
40-50 cm	22%	60%
50-60 cm	10%	2%
60-70 cm	33%	11%
80-90 cm	2%	10%

Table 2: Mean values and uncertainties of behavioral parameters

runs	10000		Objective Function				
threshold	0.1%		MAE($Q^{1/2}$)		MAE($C^{1/2}$)		
Parameter	Inferior Bound	Superior Bound	Mean optimal parameter value	Uncertainty (%)	Mean optimal parameter value	Uncertainty (%)	Unit
f_{fast} KRN	0.1	0.9	0.865	2.8			1
f_{fast} KBZ	0.1	0.9	0.229	36.84			1
α_{fast}	0.01	0.1	0.0252	11.22			d^{-1}
α_{slow}	0.001	0.01	0.0079	13.42			d^{-1}
$V_{im,fast}$	100	4000			2354	11.01	mm
$V_{im,slow}$	100	20000			16032	7.22	mm
R_c KRN	0	6			0.1728	70.21	10^{-2} kg N.ha^{-1}.d^{-1}
R_c KBZ	0	6			3.0766	16	10^{-2} kg N.ha^{-1}.d^{-1}

Table 3: Comparison of groundwater store concentrations in 1992 imposed for the model calibration and with the 1965-2012 simulation using the mean behavioural parameter set.

Concentration in GW store in 1992	Fast store		Slow store	
	calibration	Simulation 1965-2012	Calibration	Simulation 1965-2012
Kerrien	50	59.24	25	29.62
Kerbernez	95	61.17	120	125.8

Table 4: Half Nitrogen Recovery times and associated standard deviations among the range of behavioral sets and for each of the three input pulse dates, and for all the 30 simulations

Pulse	**Volume (mm) of rainfall from tpulse to tpulse+8 years**	**Kerrien**		**Kerbernez**	
		HNRT (y)	cv %	HNRT (y)	cv %
1	7813	4.8	11	12	15
2	8684	3.8	9	10	17
3	9225	3.4	8	10	22
All simulations		4.0	18.5	10.7	19.8

Figure 1: Localization of the study site and the monitoring points

Figure 2: Scheme of the modeling procedure using Burns and ETNA models

Figure 3: Time series of annual N available for leaching estimated from linear trend adjustment (1965-1991) and from yearly farm surveys (1992-2012) in Kerrien (a) and Kerbernez (b) catchments.

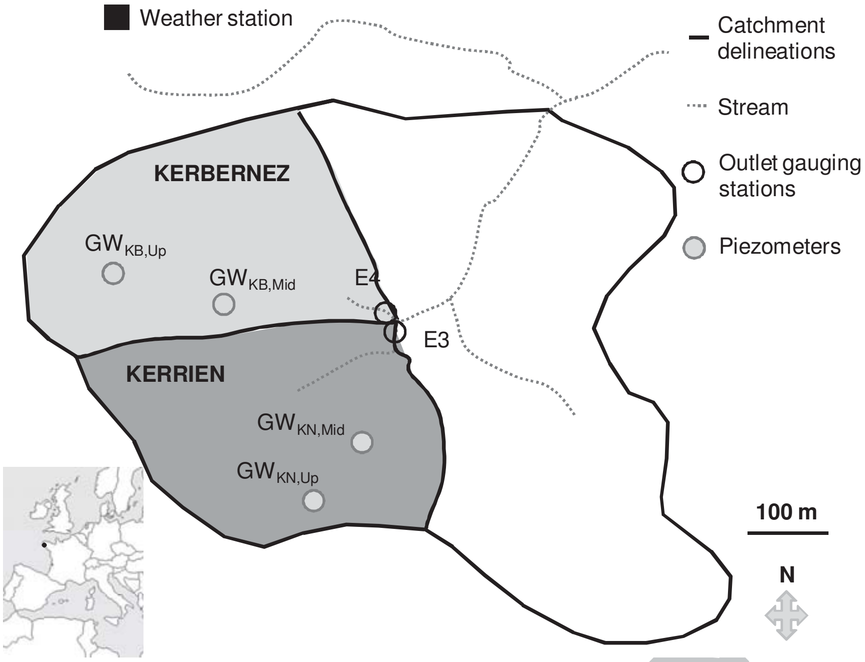
Figure 4: Dotty plots of combined likelihood values and behavioral (CLopt) sets depending on (a) hydrological parameters and (b) on parameters related to nitrogen transfer and transformation.

Figure 5: Simulated and observed discharge (a, b) and nitrate concentration (c, d, in mg of NO_3/l) at the outlets of Kerrien (a, c) and Kerbernez (b, d). BS are the results corresponding to behavioral parameter sets and mean BS are the results obtained from mean behavioral parameter set values.

Figure 6: Simulated & observed water table depth (a, b: *Z sim*, $GW_{KN,Up}$ and $GW_{KB,Up}$ are the groundwater depths respectively simulated, measured on Kerrien and Kerbernez upslope piezometers) and nitrates concentration (c, d: C_{FAST}, C_{SLOW}, $GW_{KN,Up}$ and $GW_{KN,Mid}$, $GW_{KB,Up}$ and $GW_{KB,Mid}$ are the groundwater concentrations respectively simulated in fast and slow stores, and, measured on upslope and midslope piezometers on Kerrien and Kerbernez) in groundwater of Kerrien (la, c) and Kerbernez (b, d) catchments. Simulation results correspond to the mean behavioral parameter set.

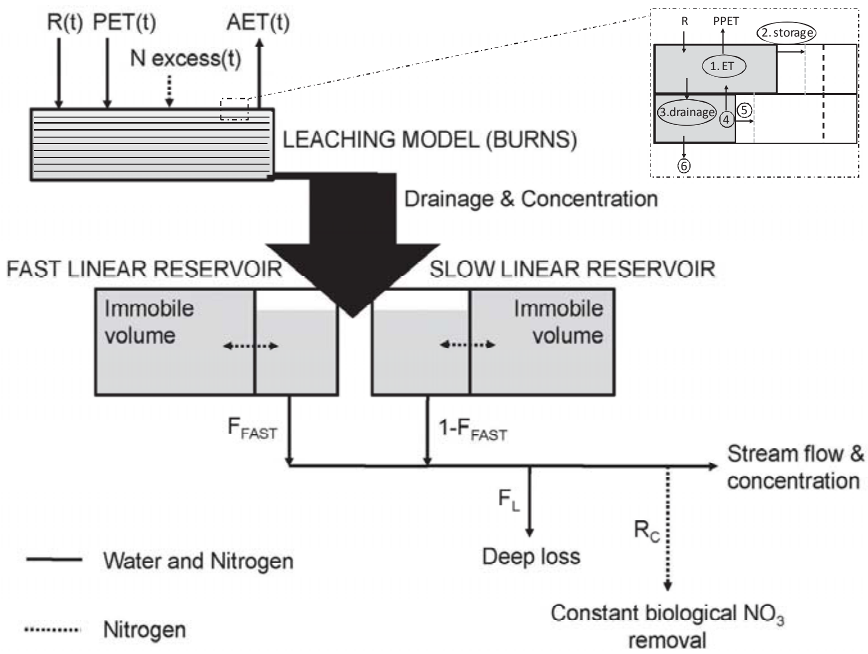
Figure 7: Long term trends simulation from 1965 to 2012: simulated and measured stream flow (a, b) & stream NO_3 concentration (c, d), and NO_3 concentration in groundwater reservoirs (e, f) on Kerrien (a ,c, e) and Kerbernez (b, d, f) catchments.

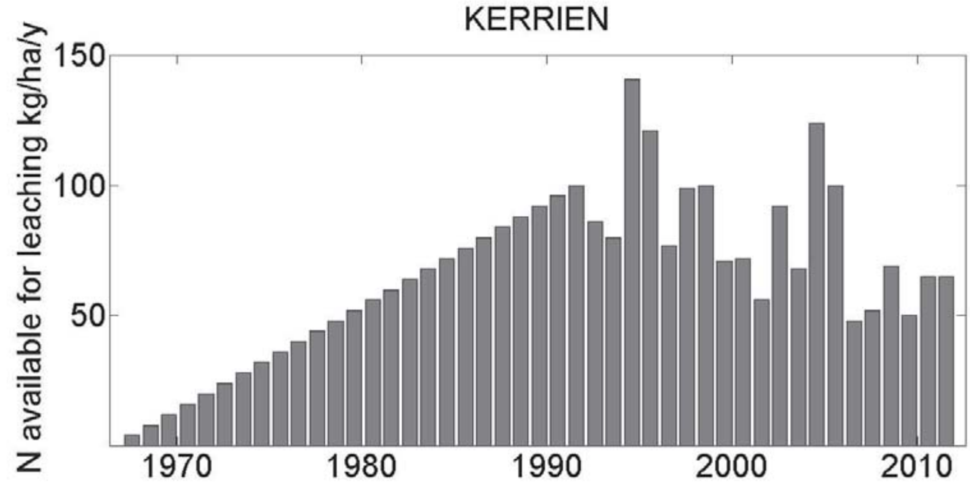
Figure 8: Evolution with time of the cumulated fraction of tracer output flux for the behavioural parameter sets for the three different dates of pluse input application (pulses 1 to 3) in Kerrien (a) and Kerbernez (b) catchments. Cumulated rainfall in the 8 years following the input date increase from pulse 1 to pulse 3 (see Table 4). Vertical dashed lines show the half nitrogen recovery time (HNRT) for each case.

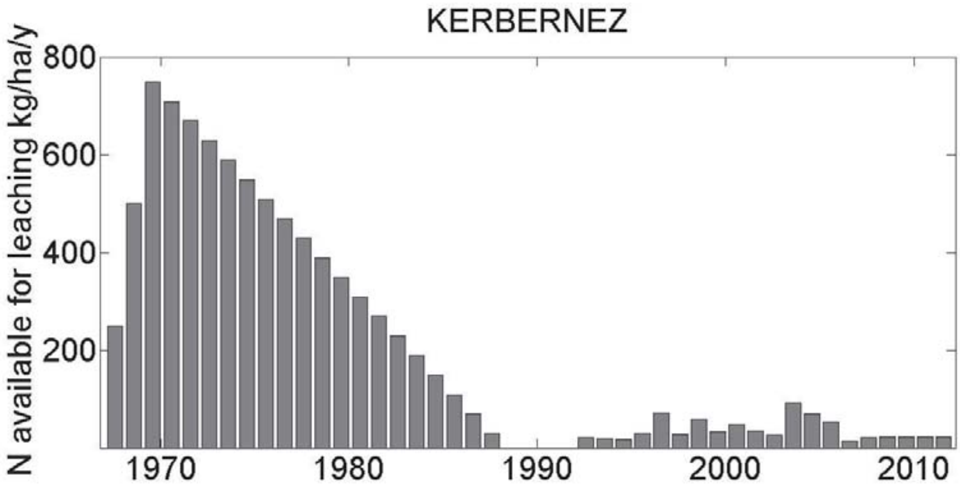

Weather station
Catchment delineations
Stream
Outlet gauging stations
Piezometers
KERBERNEZ
GW KB,Up
GW KB,Mid
E4
E3
KERRIEN
GW KN,Mid
GW KN,Up
100 m
N

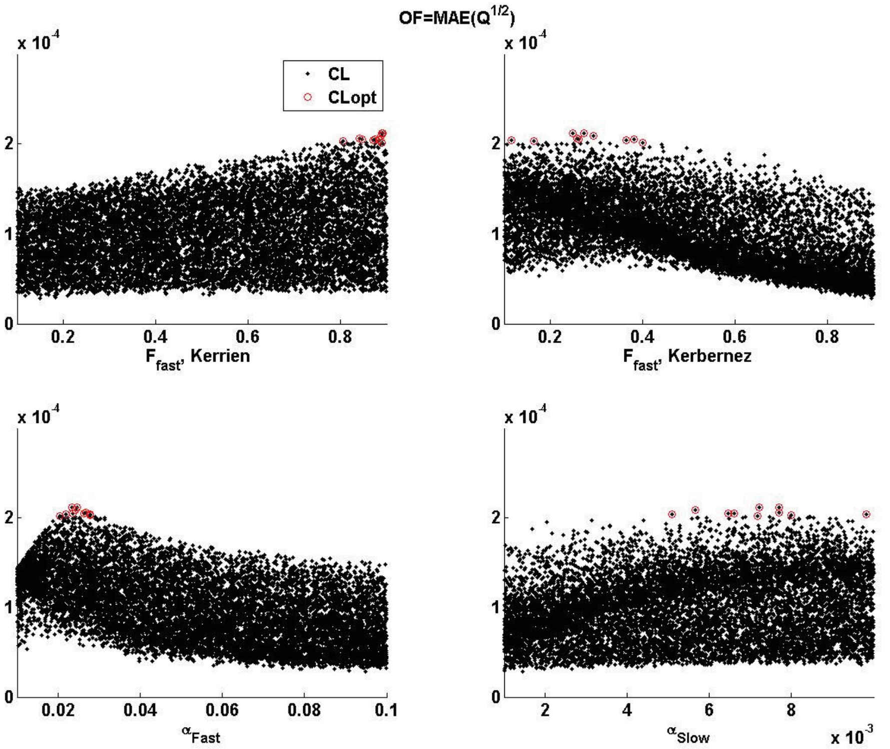
1

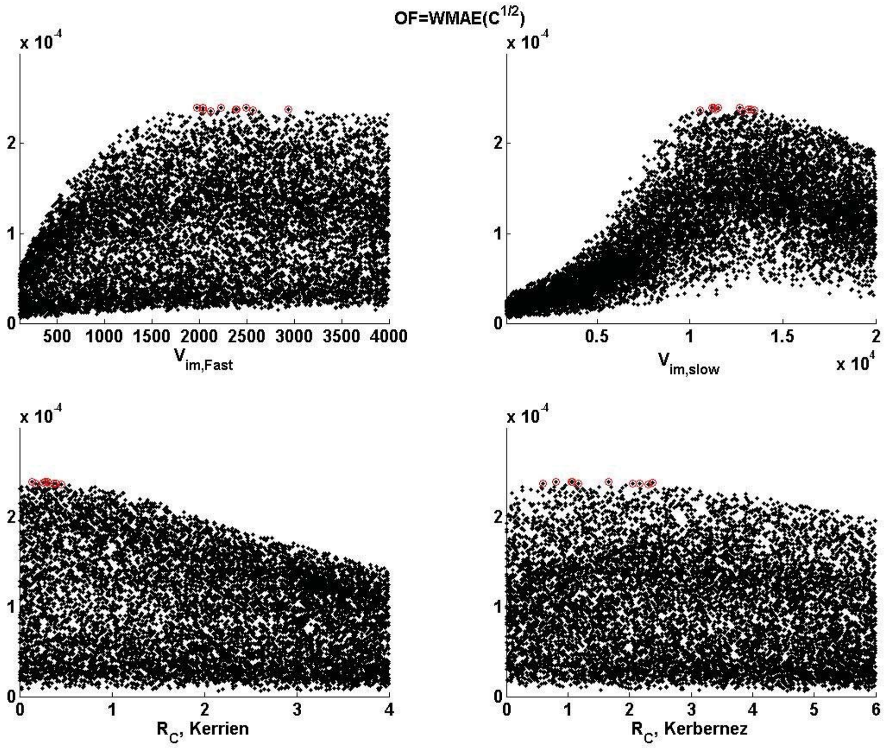
2

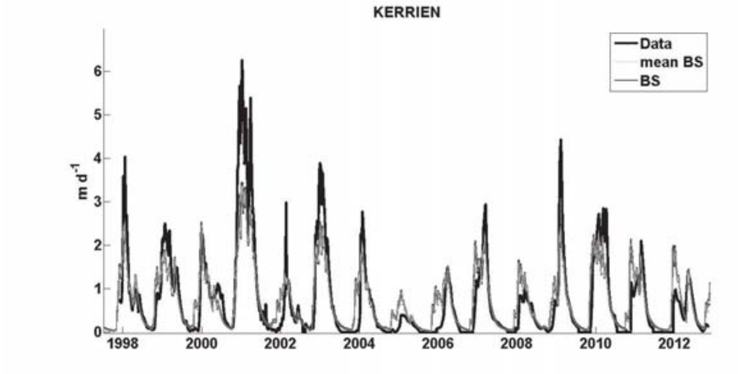

R(t)
PET(t)
AET(t)
N excess(t)
LEACHING MODEL (BURNS)
R
PPET
2. storage
1. ET
3.drainage
4
5
6
Drainage & Concentration
FAST LINEAR RESERVOIR
SLOW LINEAR RESERVOIR
Immobile volume
Immobile volume
F_{FAST}
$1\text{-}F_{FAST}$
Stream flow & concentration
F_L
Deep loss
R_C
Water and Nitrogen
Nitrogen
Constant biological NO_3 removal

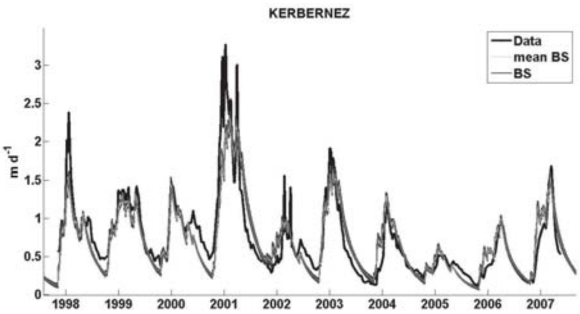

KERRIEN
N available for leaching kg/ha/y
150
100
50
1970
1980
1990
2000
2010

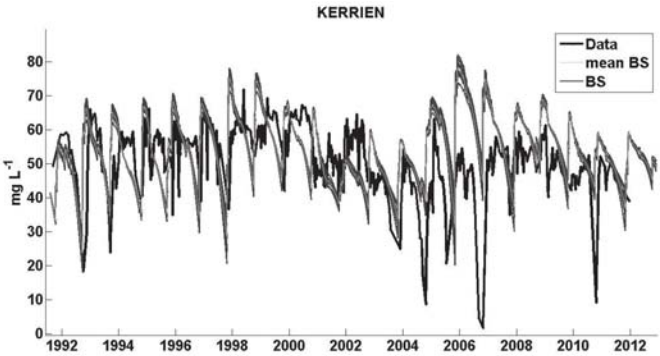

KERBERNEZ
N available for leaching kg/ha/y
800
600
400
200
1970
1980
1990
2000
2010

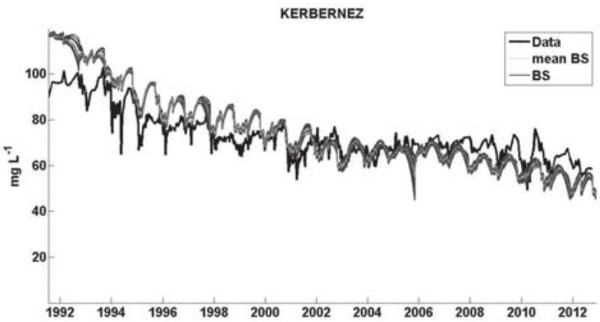

OF=MAE(Q^1/2)
x 10^-4
CL
CLopt
F_fast, Kerrien
F_fast, Kerbernez
α_Fast
α_Slow
x 10^-3

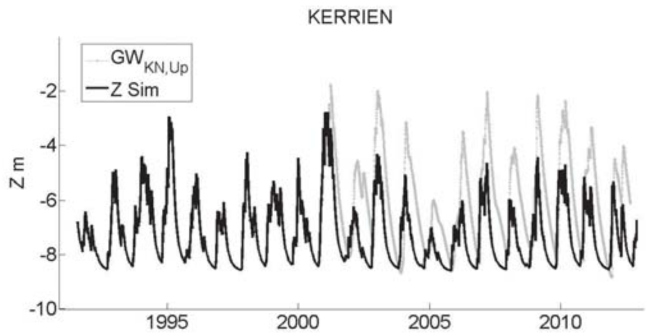

OF=WMAE(C^1/2)
x 10^-4
V_im,Fast
V_im,slow
x 10^4
R_C, Kerrien
R_C, Kerbernez

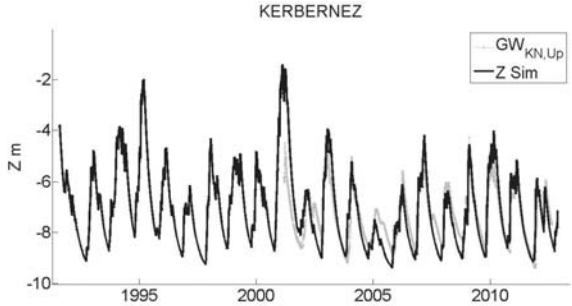

KERRIEN
Data
mean BS
BS
m d-1
0
1
2
3
4
5
6
1998
2000
2002
2004
2006
2008
2010
2012

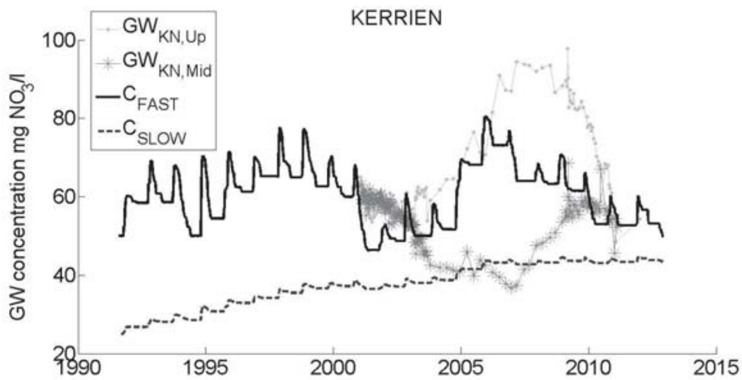

KERBERNEZ
Data
mean BS
BS
m d-1
0
0.5
1
1.5
2
2.5
3
1998
1999
2000
2001
2002
2003
2004
2005
2006
2007

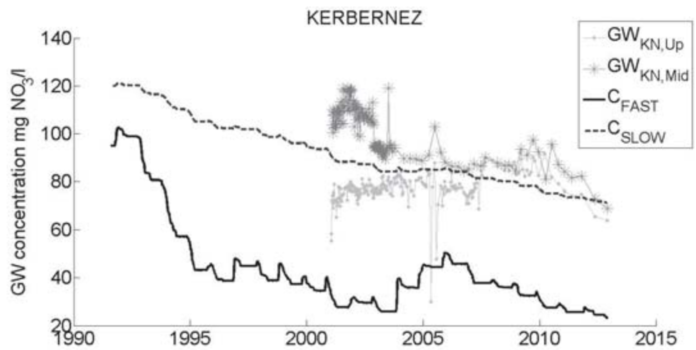

KERRIEN
Data
mean BS
BS
mg L-1
0
10
20
30
40
50
60
70
80
1992
1994
1996
1998
2000
2002
2004
2006
2008
2010
2012

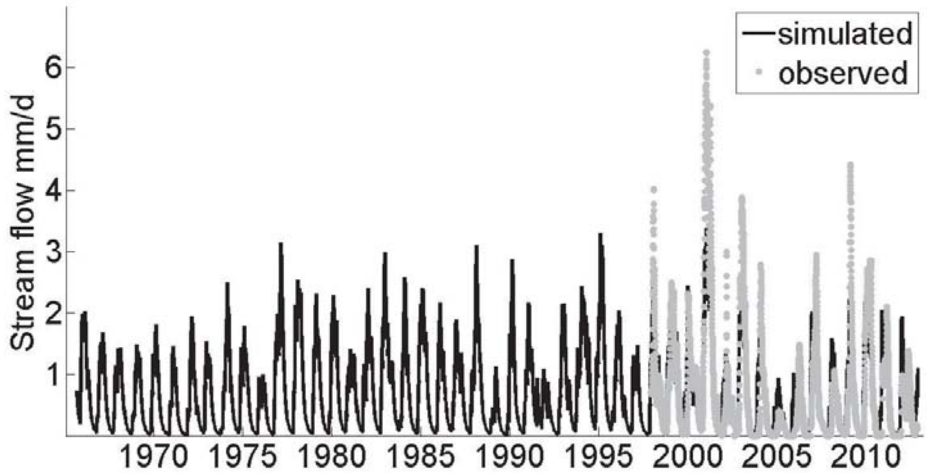

KERBERNEZ
Data
mean BS
BS
mg L-1
20
40
60
80
100
1992
1994
1996
1998
2000
2002
2004
2006
2008
2010
2012


KERRIEN
GW KN,Up
Z Sim
Z m
-2
-4
-6
-8
-10
1995
2000
2005
2010

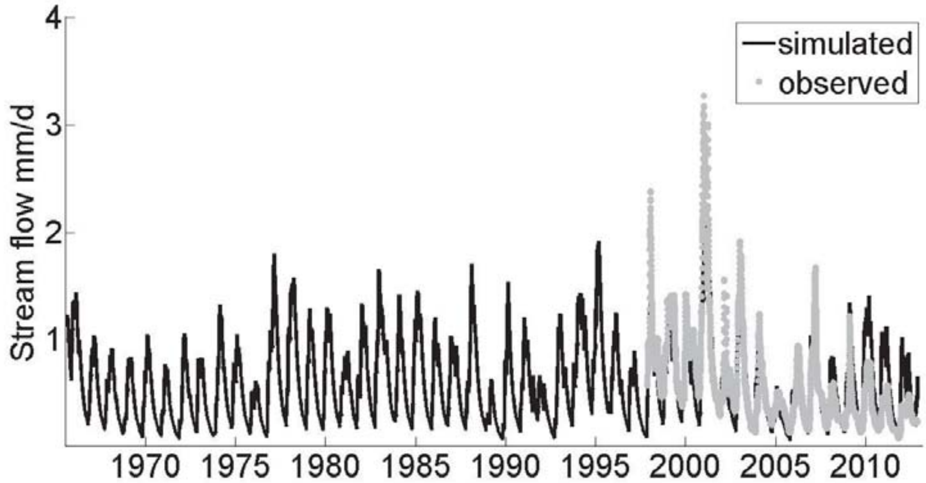

KERBERNEZ
GW KN,Up
Z Sim
Z m
-2
-4
-6
-8
-10
1995
2000
2005
2010


KERRIEN
GW KN,Up
GW KN,Mid
C FAST
C SLOW
GW concentration mg NO3/l
100
80
60
40
20
1990
1995
2000
2005
2010
2015

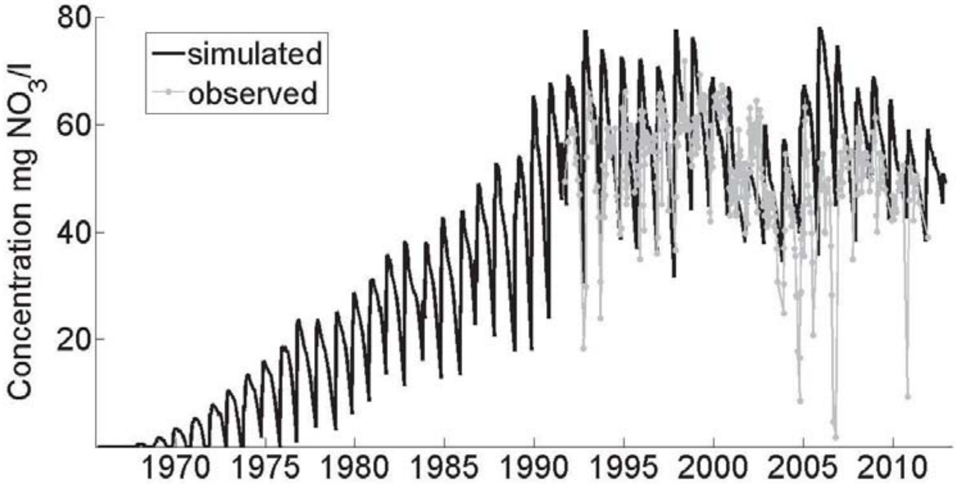

KERBERNEZ
GW KN,Up
GW KN,Mid
C FAST
C SLOW
GW concentration mg NO3/l
140
120
100
80
60
40
20
1990
1995
2000
2005
2010
2015


Stream flow mm/d
simulated
observed
1970 1975 1980 1985 1990 1995 2000 2005 2010

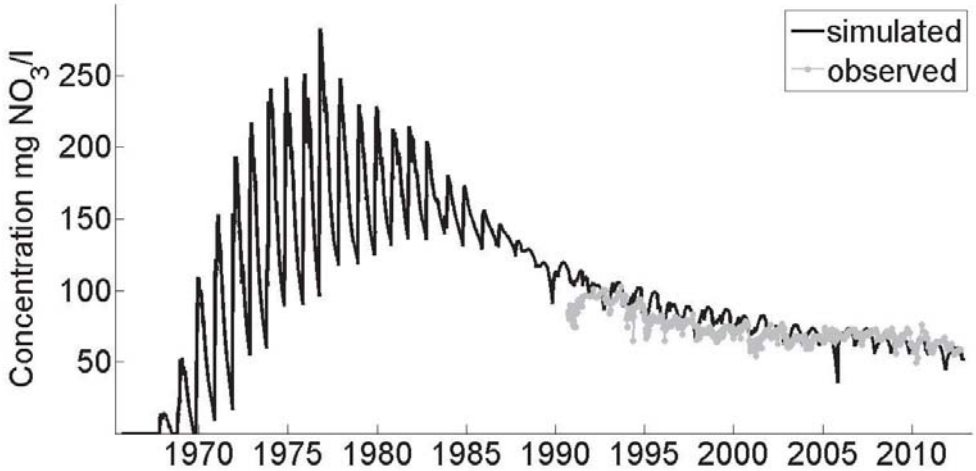
1

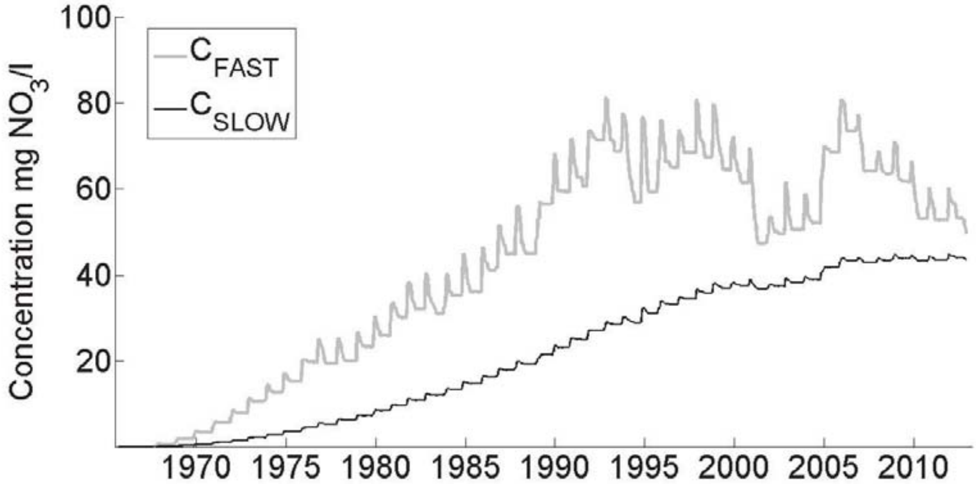

Stream flow mm/d
simulated
observed
1970 1975 1980 1985 1990 1995 2000 2005 2010

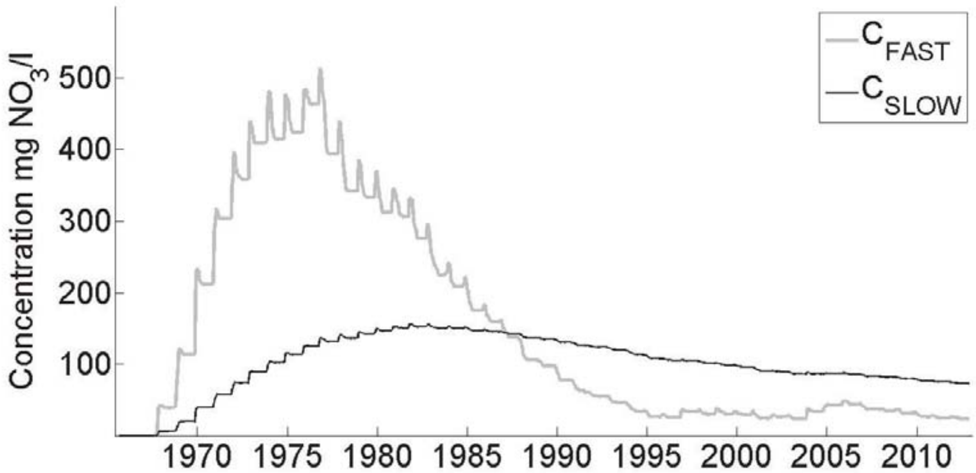
2

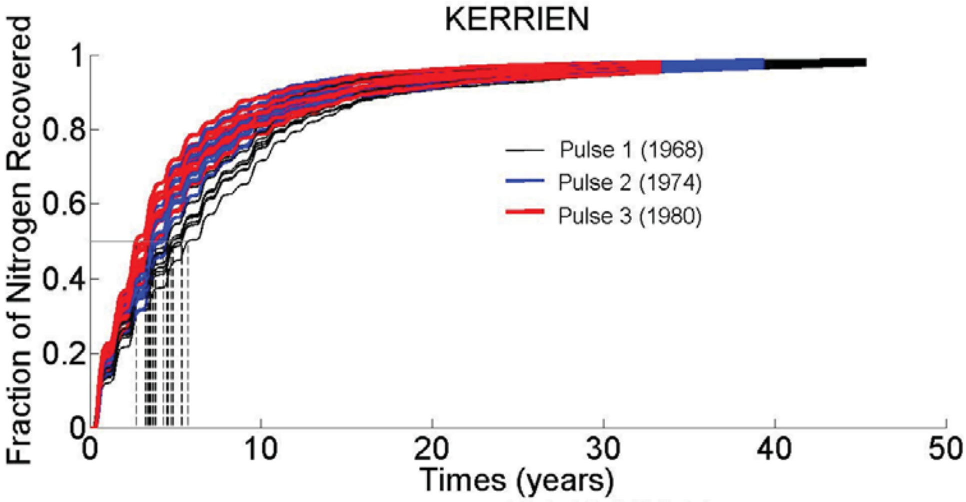

Concentration mg NO3/l
simulated
observed
1970 1975 1980 1985 1990 1995 2000 2005 2010

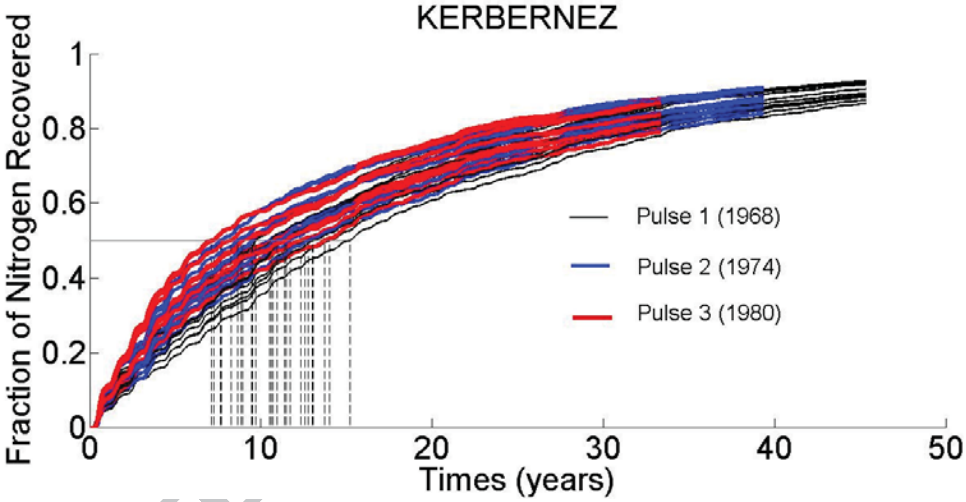
3


simulated
observed
Concentration mg NO3/l
250
200
150
100
50
1970 1975 1980 1985 1990 1995 2000 2005 2010


C FAST
C SLOW
Concentration mg NO3/l
100
80
60
40
20
1970 1975 1980 1985 1990 1995 2000 2005 2010


C FAST
C SLOW
Concentration mg NO3/l
500
400
300
200
100
1970 1975 1980 1985 1990 1995 2000 2005 2010


KERRIEN
Fraction of Nitrogen Recovered
0
0.2
0.4
0.6
0.8
1
0
10
20
30
40
50
Times (years)
Pulse 1 (1968)
Pulse 2 (1974)
Pulse 3 (1980)


KERBERNEZ
Fraction of Nitrogen Recovered
0
0.2
0.4
0.6
0.8
1
0
10
20
30
40
50
Times (years)
Pulse 1 (1968)
Pulse 2 (1974)
Pulse 3 (1980)

Highlights

- we used stream nitrate concentration to estimate transit time in catchments
- we calibrated a conceptual lumped model on two paired catchments using GLUE
- the model simulated reasonably nitrate patterns in stream and groundwater
- transit time estimations were consistent with previous studies in the same site
- transit time was as sensitive to climate variations as to parameter uncertainty